

INFRARED MULTIPHOTON AND COLLISION INDUCED DISSOCIATION
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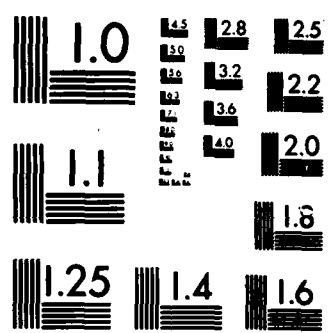
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Collision induced dissociation and infrared multiphoton dissociation of ions formed in di- and triethylamine, di- and tri-n-propylamine, and diisopropylamine were investigated by Fourier transform ion cyclotron resonance mass spectrometry. Molecular ions of all amines except di-n-propylamine produced similar fragment ions when subjected to either dissociation technique. The initial fragmentation involved C-C bond cleavage, loss of an alkyl radical, and formation of an immonium ion. Subsequent fragmentations of the immonium ions produced by both dissociation mechanisms involved McLafferty type rearrangements and loss of alkenes. The molecular ion of di-n-propylamine fragmented by a different mechanism when subjected to infrared irradiation. Protonated molecules of di- and tri-n-propylamine yielded C₃H₆⁺ and an ammonium ion upon infrared multiphoton dissociation, while protonated molecules of the other amines did not dissociate using this technique. Collision induced dissociation, on the other hand, produced fragmentation for all protonated molecules. Explanation of the different fragmentations observed for the two dissociation techniques is

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given in terms of a mechanism involving a tight transition state for protonated di- and tri-n-propylamine dissociation. *Keywords: → to field 8*

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Infrared Multiphoton and Collision Induced
Dissociation Studies of Some Gaseous Alkylamine Ions

by

C. H. Watson, G. Baykut, M. A. Battiste, and J. R. Eyler

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Infrared Multiphoton and Collision Induced Dissociation

Studies of Some Gaseous Alkylamine Ions.

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SUMMARY

Collision induced dissociation and infrared multiphoton dissociation of ions formed in di- and triethylamine, di- and tri-n-propylamine, and diisopropylamine were investigated by Fourier transform ion cyclotron resonance mass spectrometry. Molecular ions of all amines except di-n-propylamine produced similar fragment ions when subjected to either dissociation technique. The initial fragmentation involved $C_{\alpha}-C_{\beta}$ bond cleavage, loss of an alkyl radical, and formation of an immonium ion. Subsequent fragmentations of the immonium ions produced by both dissociation mechanisms involved McLafferty type rearrangements and loss of alkenes. The molecular ion of di-n-propylamine fragmented by a different mechanism when subjected to infrared irradiation. Protonated molecules of di- and tri-n-propylamine yielded C_3H_6 and an ammonium ion upon infrared multiphoton dissociation, while protonated molecules of the other amines did not dissociate using this technique. Collision induced dissociation, on the other hand, produced fragmentation for all protonated molecules. Explanation of the different fragmentations observed for the two dissociation techniques is given in terms of a mechanism involving a tight transition state for protonated di- and tri-n-propylamine dissociation.

INTRODUCTION

Infrared multiphoton dissociation (i.r.m.p.d.) of gaseous ions was first observed using an ion cyclotron resonance (i.c.r.) mass spectrometer and a low power continuous wave (c.w.) CO₂ laser [1]. A recent review [2] summarizes most experimental results through 1983. The i.c.r. technique has several advantages for studying i.r.m.p.d. Foremost among these is the ability to trap ions for long periods of time [3] to allow absorption of many infrared photons; often 5-20 photons must be absorbed before dissociation occurs [2]. With the development of Fourier transform ion cyclotron resonance (f.t.i.c.r.) [4] mass spectrometry it is now possible to detect simultaneously an entire mass spectrum, greatly facilitating the study of different photodissociation pathways. Such photodissociation pathways resulting from visible and ultraviolet (u.v.) irradiation have proven quite useful for structure elucidation of gaseous ions [5]. Recent results from this laboratory have demonstrated the utility of i.r.m.p.d. for solving gas phase ionic structure problems, most notably for isomeric differentiation [6].

Collision induced dissociation (c.i.d.) is the most widely employed mass spectrometric technique for ion structure determination [7]. Collisions of ions with (usually) inert target molecules can produce excited ions which lose excess energy by dissociating. While quadrupoles and sector type mass spectrometers have been used for most c.i.d. experiments to date, the technique has recently been developed as a standard analytical tool on f.t.i.c.r. mass spectrometers [8] as well.

In earlier studies [6] of some oxygen-containing hydrocarbon systems, primarily esters and ethers, the sole fragment produced by i.r.m.p.d. was always the same as the most intense ion observed following c.i.d. While such behavior would be expected for many ionic systems, it should not hold true in

all cases. The relatively slow excitation process in i.r.m.p.d. experiments leads to dissociation via the channel of lowest activation energy. In c.i.d. a range of internal energies is imparted to an ion during the short collision duration, and of the resulting fragment ions, the one of highest intensity need not be obtained via the pathway of lowest activation energy. This is particularly to be expected if substantial rearrangement occurs during the fragmentation, i.e. if the entropy of activation is high. Quite significant differences between c.i.d. and i.r.m.p.d. have been observed for alkylamine ions, and the results of applying the two dissociation techniques to this class of ions are reported here.

The only bond cleavage observed during earlier i.r.m.p.d. investigations [6] involved C-O, and not C-C or C-H bonds. Available thermochemical data showed that these were the weakest bonds in the ions under study. Thus the dissociation of lowest overall endothermicity (corresponding to breaking the weakest bond in the ion) correlated directly with the dissociation pathway with lowest activation energy (observed in i.r.m.p.d. experiments). Extension of the validity of this behavior to nitrogen-containing hydrocarbons was sought, to see if C-N bonds would again cleave preferentially to C-C bonds.

Infrared multiphoton dissociation of triethyl- and benzylamine ions produced by multiphoton ionization has been reported [9,10], and metastable ions produced by multiphoton ionization have been compared to those obtained using electron impact ionization [11]. One other i.r.m.p.d. study [12] of the ethylisopropylammonium ion gave useful mechanistic information about the ethylisopropylamine proton-transfer system. The present work reports i.r.m.p.d. and c.i.d. results for molecular, protonated, and fragment ions of various tri- and di- n-propyl-, isopropyl-, and ethylamines. Results for i.r.m.p.d. and c.i.d. of the various alkylamines are discussed in light of the

earlier studies [9-12].

EXPERIMENTAL

Figure 1 shows the experimental apparatus used for i.r.m.p.d. studies. The CO₂ laser beam was reflected from two gold plated glass mirrors through a ZnSe window into the vacuum system of a modified Nicolet FT/MS-1000 mass spectrometer. For monitoring laser power and wavelength a mirror supported by a kinematic mount was inserted into the beam path. This reflected the laser beam to a Ge beam splitter which allowed it to be directed to both a power meter and a spectrum analyzer. For the work reported here a fixed wavelength (10.61 μ m) and high output power (ca. 50 W measured at the laser) were used.

The 2.54 cm cubic f.t.i.c.r. analyzer cell was modified by adding a 15 mm diameter hole covered by wire mesh to one transmitter plate (see Figure 2). This modification caused no significant deterioration of the ion signal. The actual laser irradiance inside the cell was difficult to determine since multiple internal reflections from the polished stainless steel cell plates are possible. To estimate laser power entering the cell, the cell mounting flange (including the ZnSe window, see Fig. 1), support rod, and cell were removed from the vacuum chamber. The transmitter plate opposite the one through which the laser enters the cell was removed, and the laser was reflected from the Au mirrors, passed through the ZnSe window, reflected from the cell beam reflector (see Fig. 2) and passed through the transmitter plate mesh while outside of the vacuum system. The laser power exiting the (open) analyzer cell under these conditions, identical to those used in actual experimentation, was 20 W (approximately a factor of 2.5 less than the direct output of the laser). Assuming one internal reflection from the transmitter plate which had been removed for the above measurement, and a 1 cm² cross sectional area for the laser beam, an estimate of the actual irradiance to

which the ions were subjected is 40 W/cm^2 . For favorable cases 100 percent dissociation was observed, indicating complete overlap of the laser beam and the trapped ion cloud.

A typical i.r.m.p.d. experiment consisted of ion formation by electron impact (50 eV for 5 ms) followed by a reaction delay (0-1000 ms) to build up a significant concentration of protonated molecules via fragment ion/molecule reactions. The reaction delay was not necessary when molecular ion dissociation was being investigated. The ion of interest was next isolated by ejection of all other ions, followed by gated laser irradiation of 200-2000 ms. Immediately after laser irradiation the ions were detected.

Collision induced dissociation experiments were carried out similarly to those involving i.r.m.p.d. except that an oscillating voltage with a frequency equal to the cyclotron frequency of the ion to be accelerated applied to opposing cell plates (typically for 100 μs) instead of laser irradiation was used to excite the ion to higher translational energies and a collision time of typically 10 ms was then allowed for dissociation. Sample pressure was maintained at ca. $4.0 \times 10^{-6} \text{ N/m}^2$ (3×10^{-8} torr), as measured on an ionization gauge. Argon or xenon was added as collision gas until the total pressure was in the $7\text{--}13 \times 10^{-5} \text{ N/m}^2$ ($5\text{--}10 \times 10^{-7}$ torr) range. The maximum kinetic energy to which ions can be accelerated in f.t.i.c.r. c.i.d. experiments before they strike the walls of the analyzer cell is given by [8],

$$K.E._{\text{max}} = e^2 r^2 B^2 / (2m)$$

where e is the charge of an electron; r is the cyclotron radius; B is the magnetic field; and m is the mass of the ion. In the experiments reported here, $B = 3\text{ T}$, $r = 1.27 \text{ cm.}$, and thus $K.E._{\text{max}} = 486 \text{ eV}$ for protonated tripropylamine (m/z 144). To maximize the intensities of observed fragment ions most c.i.d. experiments were carried out by exciting parent ions to

kinetic energies very near the maximum allowable (ca. 400-800 eV depending on ion mass).

All chemicals were obtained commercially and sample purity was determined by electron impact mass spectrometry. No further sample purification was necessary except for several freeze-pump-thaw cycles to remove noncondensable gases.

RESULTS AND DISCUSSION

General

Both the i.r.m.p.d. and c.i.d. of molecular ions, protonated molecules, and selected fragment ions of tri-n-propyl-, triethyl-, di-n-propyl-, diisopropyl-, and diethylamine were studied. Results are listed in Table I. For molecular ions C-C bond cleavage and production of an immonium ion were observed for both means of dissociation. Protonated molecules, however, showed somewhat different behavior. Their dissociation generally involved C-N bond cleavage with some type of rearrangement when induced by laser irradiation, while c.i.d. proceeded via C-C bond cleavage and production of an immonium ion, or C-N bond cleavage and formation of an alkyl ion. Daughter ions, produced by either i.r.m.p.d. or c.i.d., fragmented further, typically by a mechanism similar to that which led to their formation.

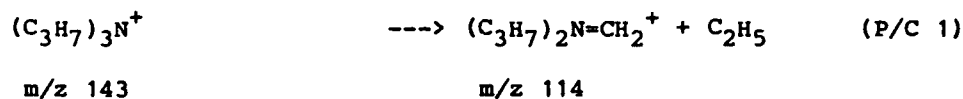
Detailed discussion of all dissociations is given below. Reactions observed only in i.r.m.p.d. are labelled with a "P" (e.g. P 1), reactions observed only in a c.i.d. with a "C" (e.g. C 2), and reactions observed in both processes with "P/C" (e.g. P/C 3).

Molecular Ions

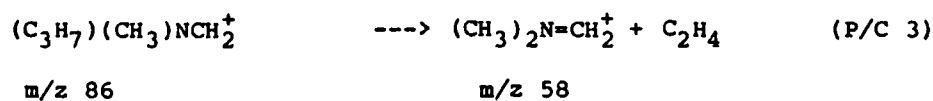
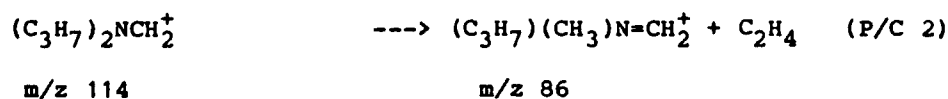
Both i.r.m.p.d. and c.i.d. were observed for the molecular ions produced by electron impact on tri-n-propyl-, triethyl-, di-n-propyl-, diisopropyl-, and diethylamine. In every case i.r.m.p.d. produced only one fragment, which,

except for di-n-propylamine, was also the most intense ion observed following c.i.d. For most cases production of the primary fragment ion could be explained by C-C bond cleavage, with formation of a stable immonium ion. Further dissociation of major fragments, usually producing yet another immonium ion, was generally observed. However, a different mechanism must be used to explain secondary fragmentations than that which holds for production of the original immonium ion. For the fragment ions dissociation is postulated to occur via a mechanism involving hydrogen transfer and C-N bond cleavage.

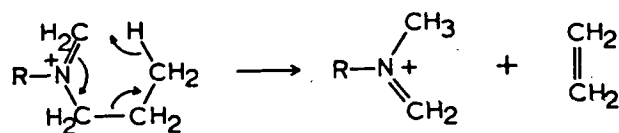
The molecular ion of tripropylamine exhibits $C_{\alpha}-C_{\beta}$ bond cleavage to produce a m/z 114 ion (presumably of an immonium structure) during both i.r.m.p.d. and c.i.d.:



The same subsequent fragmentation of this immonium ion is produced by both c.i.d. and i.r.m.p.d., but dissociation in this case occurs via a mechanism different from that which holds for the molecular ion. The m/z 114 ion dissociates to produce a m/z 86 ion, which in turn dissociates further to produce a m/z 56 ion.



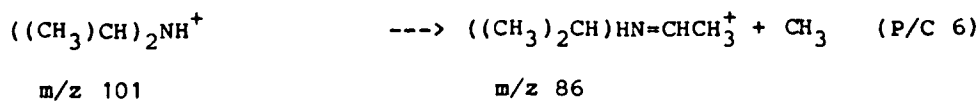
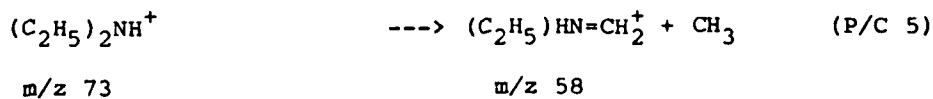
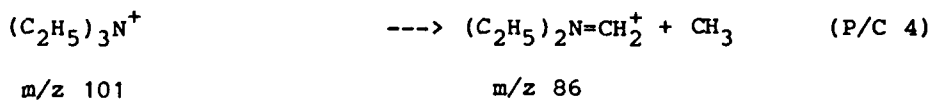
Reactions (P/C 2) and (P/C 3) are both postulated to involve γ -hydrogen transfer followed by ethene expulsion via a McLafferty type rearrangement [13].



Scheme I

Similar rearrangements and fragmentations observed in slow metastable decompositions of immonium ions have been discussed by Bowen [14]. Some additional fragments, listed in Table 1, were also produced by c.i.d. of the m/z 86 ion.

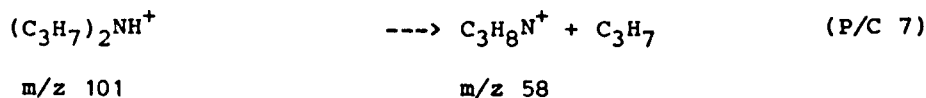
Molecular ions of triethyl-, diethyl-, and diisopropylamine all fragment by i.r.m.p.d. and c.i.d. through a mechanism similar to that observed for tri-n-propylamine: C-C bond cleavage with formation of alkyl radicals and immonium ions.



No further photodissociation of the m/z 86 immonium ion produced in reaction (P/C 4) was observed, consistent with the γ -hydrogen transfer mechanism depicted in Scheme I. The activation energy barrier for direct C-N bond cleavage apparently is too high to be overcome during the i.r.m.p.d. process.

Photodissociation of the triethylamine ion using a pulsed CO_2 laser has been reported by Haas and Lifshitz [11]. Fragmentation as shown in reaction (P/C 4) was seen. Subsequent dissociation of the m/z 86 photoproduct ion to form a m/z 58 ion, which fragmented further to produce m/z 30 and m/z 28 ions was seen by those workers. Similar photo-fragment ion dissociation was not observed in this work, probably because the relatively low irradiance of the c.w. CO_2 laser was not sufficient to excite these ions over apparently high barriers to dissociation.

Dissociation of the molecular ion of di-n-propylamine cannot be explained by a mechanism similar that used for the other molecular ions studied. A m/z 58 ion was produced by both i.r.m.p.d. and c.i.d.

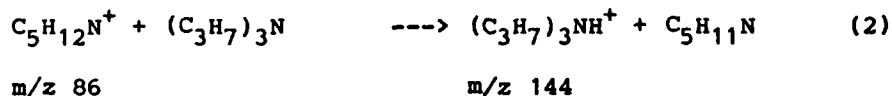
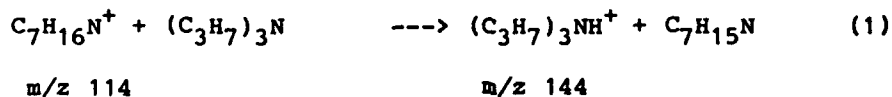


The m/z 58 ion was the only fragment observed following i.r.m.p.d., but it was seen as a minor product following c.i.d., while a m/z 72 ion ($(\text{C}_3\text{H}_7)\text{HN}=\text{CH}_2^+$) was the most intense fragment, consistent with c.i.d. results for the other molecular ions (C-C bond cleavage and immonium ion formation). No detailed explanation for the different i.r.m.p.d. behavior of the di-n-propylamine molecular ion can be given at this time.

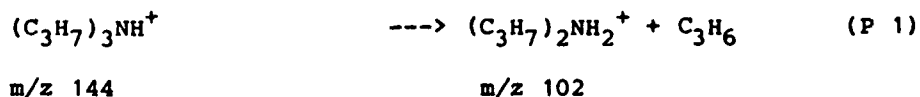
Protonated Molecules

Numerous fragment ions were formed during electron impact ionization of the alkylamines studied in this work. Proton transfer reactions of these fragments with alkylamine neutrals produced protonated molecules. Infrared laser irradiation of these ions resulted in C-N bond cleavage with hydrogen shift and loss of an alkyl group, producing an ammonium ion. In marked contrast, the major ion observed following c.i.d. was either an immonium ion resulting from C-C bond cleavage and loss of an alkyl radical, or an alkyl ion produced by C-N bond cleavage. This behavior was observed in both tri-n-propyl- and di-n-propylamine.

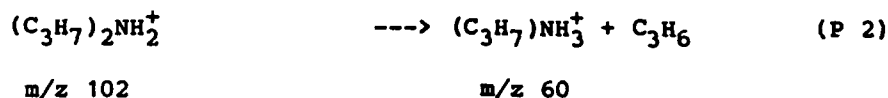
Tri-n-propylamine is protonated by ion-molecule reactions of the electron impact fragments $C_7H_{16}N^+$ and $C_5H_{12}N^+$:



When subjected to maximum laser irradiance (ca. 40 W/cm²) the protonated molecular ion fragments to produce a m/z 102 ion

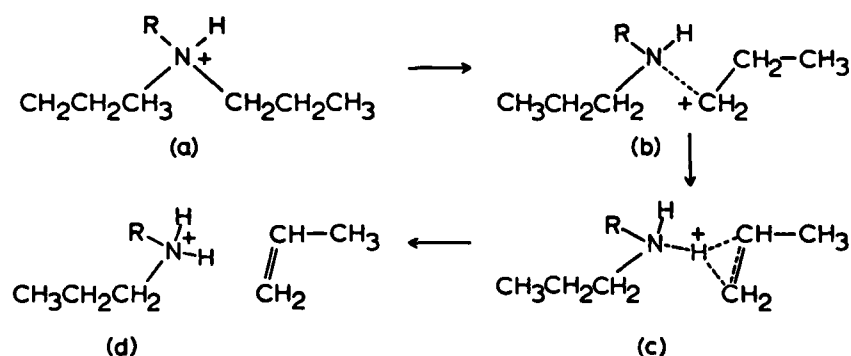


which photodissociates to produce a m/z 60 ion.



This process is assumed to occur analogously to the reaction (P 1). A m/z 102 ion was also observed in the c.i.d. spectrum as a very minor peak. Experiments at lower collision energies with a triple quadrupole mass spectrometer [15] confirmed this result.

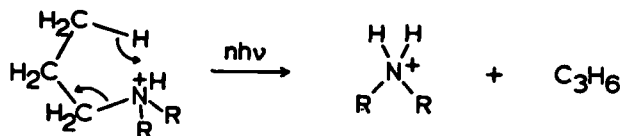
Reaction (P 1) involves cleavage of a C-N bond and transfer of a hydrogen to the nitrogen atom. Considerable evidence has been amassed by earlier workers that this dissociation occurs via a loose complex. Stretching of the C-N bond gives rise to a complex (b) in which an incipient carbonium is coordinated to an amine. Slight rearrangement in (b) leads to (c), where an amine and olefin are bound to a common proton. Dissociation of (c) then occurs, and the proton remains with the neutral of highest proton affinity, in this case the amine. This type of mechanism is discussed extensively by Moylan and Brauman [12] in explaining pulsed CO_2 laser i.r.m.p.d. of protonated ethylisopropylamine, and was also frequently invoked by Bowen [14] to explain metastable decomposition of immonium ions.



Scheme II

Alternatively, a mechanism (Scheme III) which involves C-N bond cleavage and transfer of a γ -hydrogen could explain the dissociation observed for

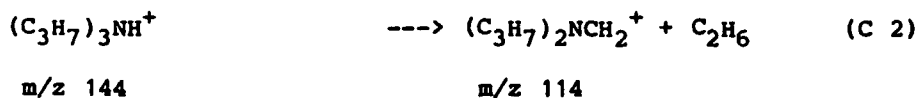
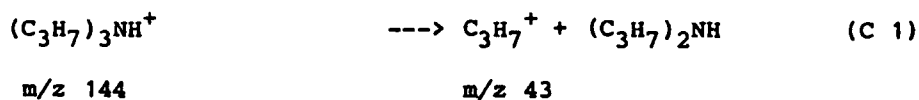
protonated tri-n-propylamine.



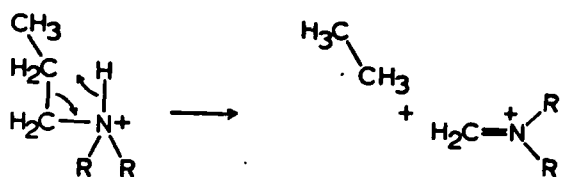
Scheme III

Further support for this mechanism is provided by experimental results for i.r.m.p.d. of protonated triethyl- and diisopropylamine. For these ions, which have no available γ -hydrogens, no significant dissociation was observed upon irradiation. However, dissociation of these ions via the proton-bridged loose complex mechanism shown in Scheme II should be almost as facile as dissociation of protonated tri-n-propylamine.

The c.i.d. of protonated tri-n-propylamine gave rise to different products than i.r.m.p.d.

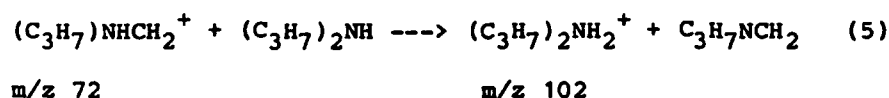
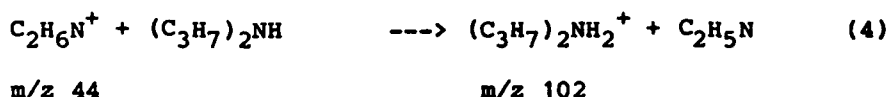
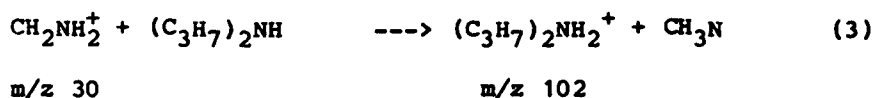


Reaction (C 1) involves a simple C-N bond cleavage and requires an overall enthalpy of 368 kJ/mol. The second reaction, however, is more complicated. A hydrogen migration from N to a beta C is necessary to form the m/z 114 immonium ion and an ethane molecule. A possible mechanism is presented in Scheme IV below.



Scheme IV

Di-n-propylamine is protonated by ion/molecule reactions involving the fragment ions CH_2NH_2^+ , $\text{C}_2\text{H}_6\text{N}^+$, and $\text{C}_3\text{H}_7\text{NHCH}_2^+$, formed by electron impact:



Protonated di-n-propylamine photodissociates by reaction (P 2) producing a m/z 60 $(\text{C}_3\text{H}_7)\text{NH}_3^+$ ion. Collision induced dissociation of protonated di-n-propylamine produces C_3H_7^+ (m/z 43) and $\text{C}_3\text{H}_7\text{NH}_3^+$ (m/z 60). Formation of the m/z 60 $\text{C}_3\text{H}_7\text{NH}_3^+$ ion is postulated as taking place via a mechanism identical to the i.r.m.p.d. of this ion shown in reaction (P 2).

No photodissociation of protonated diisopropyl- or diethylamine was observed. Since these ions contain no γ -hydrogens, the observed results are more consistent with the mechanism shown in Scheme III than that shown in Scheme II. More definitive evidence as to the importance of γ -hydrogen

transfers would be provided by study of alkylamines labeled with deuterium at that position. Limited deuterium labelling experiments were carried out by transferring a deuteron from D_3O^+ to the amines. The deuterium atom was retained on the amine after alkene loss, indicating no hydrogen transfer between the nitrogen and carbon atoms in the protonated amines. As would be expected, this type of experiment gives no information as to whether Scheme II or Scheme III is operative. The deuterium atom was lost in reaction (C2), supporting the validity of Scheme IV. Experiments involving synthesis and study of alkyl amines with deuterium on the γ -carbon in order to further establish the proposed mechanisms are currently underway.

Infrared multiphoton dissociation proceeds only via the fragmentation pathway of lowest activation energy. Collisional and radiative energy loss processes compete with absorption of infrared photons during the several hundred milliseconds of irradiation time usually required when a gated c.w. CO_2 laser is used in this process. This limits the amount of internal energy which can be deposited into an ion to ca. 160-250 kJ/mol. If the barriers to fragmentation for all pathways are higher than this range, no dissociation is observed. Such appears to be the case for protonated di- and triethylamine and diisopropylamine. For protonated di- and tri-n-propylamine, C-N bond cleavage with accompanying hydrogen transfer to the nitrogen atom, whether it takes place via Scheme II or Scheme III, has sufficiently low activation energy that it can be observed by i.r.m.p.d. Collision induced dissociation results for these two ions show formation of alkyl ions via direct C-N bond cleavage as the major fragmentation process. These fragmentations have a higher energy, but lower entropy, of activation and should be favored in c.i.d., which can impart much higher internal energies to ions than i.r.m.p.d. [16]. The fact that the only fragment ion produced by infrared irradiation is

either not formed (in protonated tri-n-propylamine dissociation) or seen only as a minor fragment (in protonated di-n-propylamine dissociation) during the c.i.d. process lends further support to the fragmentation mechanism shown in Scheme III, which involves a tight transition state. In cases where c.i.d. results only were observed (protonated di- and tri-ethylamine and diisopropylamine) the major fragment ion was often produced by a high energy process [e.g. 368 kJ/mol [17] for reaction (C 1)], attesting to the higher range of internal energies deposited in the ions during the c.i.d. process.

Earlier work from these laboratories [6] demonstrated the potential of i.r.m.p.d. for isomeric differentiation. It is interesting to note that both parent and protonated di-n-propylamine and diisopropylamine ions exhibit substantially different photodissociation behavior (Table 1). As may be seen in Table 1, c.i.d. can be used for isomeric differentiation as well.

In summary, significant differences between i.r.m.p.d. and c.i.d. were seen for protonated amines, but unprotonated molecular ions behaved similarly under both dissociation processes. In contrast to the work on oxygenated compounds where C-O bonds and not C-C bonds were broken, some of the amines in this study preferentially underwent C-C and not C-N bond cleavage. Extension of these studies to other classes of heteroatom-containing compounds is planned to further compare and contrast i.r.m.p.d. and c.i.d.

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16. C.i.d. fragmentation ratios can vary dramatically with collision energy. The results reported here correspond to energies in the range 400-800 eV. In one series of experiments involving protonated tri-n-propylamine ion kinetic energies were successively lowered to the 5-20 eV range. At these ion collision energies the m/z 102 ion, observed exclusively following i.r.m.p.d., was the major c.i.d. fragment, although quite low in intensity when compared to its formation by i.r.m.p.d. or to the m/z 43 ion formed at higher collision energies.
17. Thermochemical data cited are given in: (a) D. H. Aue and M. T. Bowers, in M. T. Bowers (Ed.), Gas Phase Ion Chemistry, Vol. 2, Academic Press, New York, 1979, P. 1. (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, Ionization Potentials Appearance Potentials and Heats of Formation of Gaseous Ions, NSRDS-NBS 26, Washington, D.C., 1969. (c) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, Energetics of Gaseous Ions, J. Phys. Chem. Ref. Data, Suppl. 1, 6, 1977.

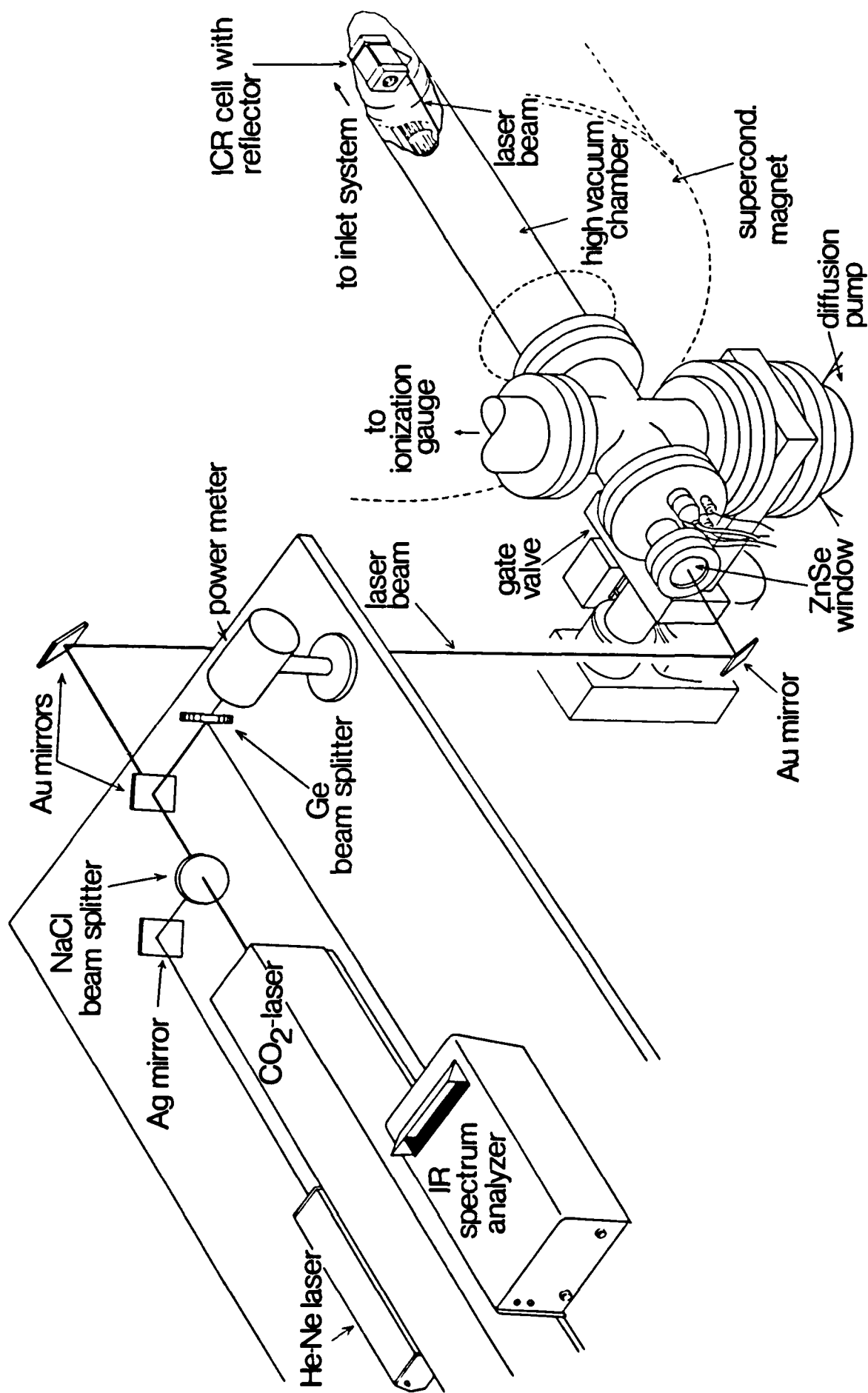
TABLE 1
I.r.m.p.d. and C.i.d. Results for Selected Alkylamines

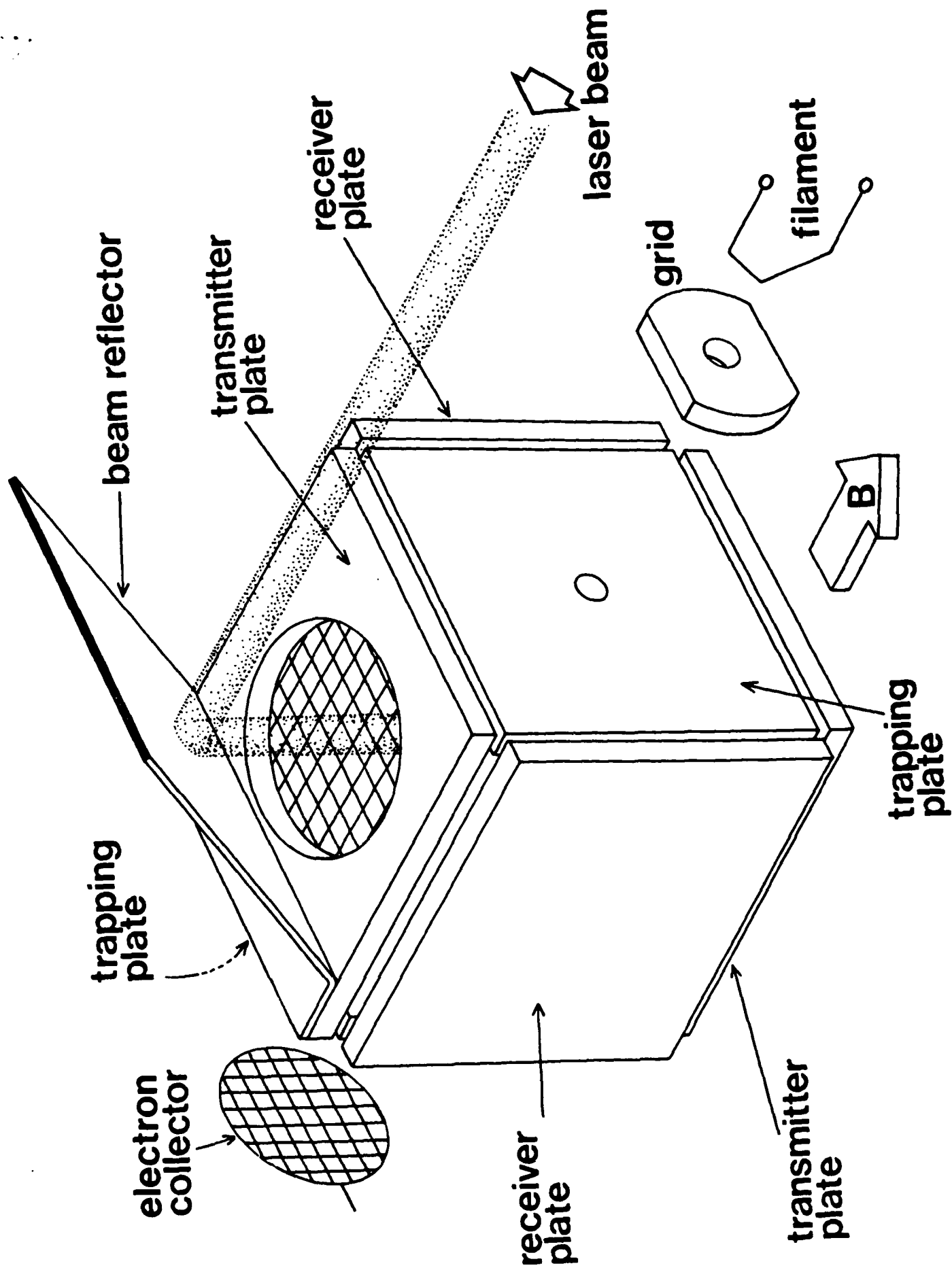
AMINE Type of Ion (Mode of Formation)	ION	i.r.m.p.d. fragments (m/z)	c.i.d. fragments (m/z)
Tripropylamine			
M ⁺ (e.i.)	(C ₃ H ₇) ₃ N ⁺ (m/z 143)	114	<u>114</u> , 86, 43
F ⁺ (i.r.m.p.d./c.i.d.)	(C ₃ H ₇) ₂ NCH ₂ ⁺ (m/z 114)	86	<u>86</u> , 43
F ⁺ (i.r.m.p.d./c.i.d.)	C ₃ H ₇ (CH ₃)NCH ₂ ⁺ (m/z 86)	58	<u>58</u> , 44, 43
M+1 ⁺ (i.m.r.)	(C ₃ H ₇) ₃ NH ⁺ (m/z 144)	102	114, <u>43</u>
F ⁺ (i.r.m.p.d.)	(C ₃ H ₇) ₂ NH ₂ ⁺ (m/z 102)	60	60, <u>43</u>
Triethylamine			
M ⁺ (e.i.)	(C ₂ H ₅) ₃ N ⁺ (m/z 101)	86	86
M+1 ⁺ (i.m.r.)	(C ₂ H ₅) ₃ NH ⁺ (m/z 102)	n.s.f.	74, <u>58</u> , 29
Di-n-propylamine			
M ⁺ (e.i.)	(C ₃ H ₇) ₂ NH ⁺ (m/z 101)	58	<u>72</u> , 58, 30, 29
M+1 ⁺ (i.m.r.)	(C ₃ H ₇) ₂ NH ₂ ⁺ (m/z 102)	60	60, <u>43</u> , 41, 30, 27
Diisopropylamine			
M ⁺ (e.i.)	((CH ₃) ₂ CH) ₂ NH ⁺ (m/z 101)	86	<u>86</u> , 44, 43, 27
M+1 ⁺ (i.m.r.)	((CH ₃) ₂ CH) ₂ NH ₂ ⁺ (m/z 102)	n.s.f.	86, 60, 44, <u>43</u>
Diethylamine			
M ⁺ (e.i.)	(C ₂ H ₅) ₂ NH ⁺ (m/z 72)	58	<u>58</u> , 30, 29
M+1 ⁺ (i.m.r.)	(C ₂ H ₅) ₂ NH ₂ ⁺ (m/z 74)	n.s.f.	58, <u>30</u> , 29

The following notation is used in Table I: M⁺ = molecular ion; M+1⁺ = protonated molecule; F⁺ = fragment ion; (e.i.) refers to ions formed by electron impact; (i.r.m.p.d./c.i.d.) refers to ions formed by either i.r.m.p.d. or c.i.d.; (i.r.m.p.d.) refers to ions formed solely by i.r.m.p.d.; (i.m.r.) refers to ions formed by ion/molecule reactions; n.s.f. = no significant fragmentation was observed (fragment peak had S:N < 2). The fragment ion of highest intensity produced by c.i.d. is underlined. High resolution experiments showed that m/z 44 fragment ions produced by c.i.d. were C₂H₆N⁺, m/z 43 ions were C₃H₇⁺, m/z 30 CH₄N⁺, m/z 29 C₂H₅⁺, and m/z 27 C₂H₃⁺.

FIGURE CAPTIONS

1. Laser table and cutaway view of relevant portions of the f.t.i.c.r. instrumentation. The He/Ne laser was used only for alignment of the CO₂ laser and the NaCl beam splitter was removed during ion irradiation.
2. Cubic i.c.r. cell modified for irradiation of trapped ions. Direction of the magnetic field (B) is as indicated.





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